

Utility of Thin-Film Solar Cells on Flexible Substrates for Space Power

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ABSTRACT

The thin-film solar cell program at NASA GRC is developing solar cell technologies for space applications which address two critical metrics: specific power (power per unit mass) and launch stowed volume. To be competitive for many space applications, an array using thin film solar cells must significantly increase specific power while reducing stowed volume when compared to the present baseline technology utilizing crystalline solar cells.

The NASA GRC program is developing two approaches. Since the vast majority of the mass of a thin film solar cell is in the substrate, a thin film solar cell on a very lightweight flexible substrate (polymer or metal films) is being developed as the first approach. The second approach is the development of multijunction thin film solar cells. Total cell efficiency can be increased by stacking multiple cells having bandgaps tuned to convert the spectrum passing through the upper cells to the lower cells.

Once developed, the two approaches will be merged to yield a multijunction, thin film solar cell on a very lightweight, flexible substrate. The ultimate utility of such solar cells in space require the development of monolithic interconnections, lightweight array structures, and ultra-lightweight support and deployment techniques.

INTRODUCTION

Future space missions are being planned which require the development of advanced solar energy conversion systems. These missions require significant improvements in specific power (power per unit mass), launch stowed volume, and environmental tolerance such as radiation resistance of the solar energy conversion system. Concepts range from large solar power satellites to nanosats.^{1,2} Solar electric propulsion is being developed for deep space missions such as the successful Deep Space 1 mission² as well as orbital transfer missions.

Photovoltaic arrays have and will continue to play a key role in the generation of power in space. The baseline photovoltaic arrays in space utilize crystalline solar cells. While crystalline solar cells have continued to evolve, missions requiring very high specific power and small launch stowed volume may not be able to be flown using crystalline solar cells. Thin film solar cells built on very lightweight substrates may be an enabling technology for future space missions by significantly increasing specific power while reducing launch stowed volume.

The leading thin film solar cell technologies are amorphous silicon, CuInSe_2 , and CdTe. While these technologies have made significant advances over the years, it may take them many years to reach the 15-20% AM0 efficiency required for many space applications. II-IV-based multijunction, thin-film, solar cells have the potential to achieve AM0 efficiencies of up to 25%.

Fabrication of a thin film solar cell is only the first step in the construction of a solar energy conversion system for use in space. Before such cells can be fully utilized in space, interconnections, array structures, support structures, and deployment techniques need to be developed that take full advantage of the lightweight, flexible nature of the thin film solar cells.

NASA GRC has an established thin film solar cell program. Working in cooperation with industry and academia, the GRC thin film program consists of research efforts in thin film solar cell modeling, thin film solar cell development on metal and polymer films, thin film solar cell system studies, and thin film solar cell array technologies.



polyimide				
top window layer				
CdSe or CdZnTe ⊅R1				
transparent conductor 🖊 R2				
encapsulant 7R3				
top window layer				
CIGS				
Mo				
polyimide				

Figure 1. 4-terminal tandem device structure.

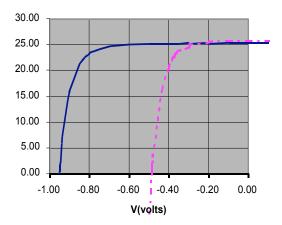


Figure 2. Simulated AM0 IV curves for a tandem device consisting of a 1.55 eV top cell and 0.95 eV bottom CIS cell. Tandem efficiency is 20.1%.

The Analysis of Microelectronic and Photonic Structures (AMPS) modelling of the CdSe or CdZnTe on CuIn_{1-x}Ga_xS₂ tandem structure (Figure 1) predicted AM0 efficiencies of near 20% as reported last year.³ The study also predicted that improvements in materials could increase the AM0 efficiency to approximately 25%. Potential AM0 efficiencies in this range makes this device a candidate for development for space applications.

As can be seen in Figure 2, the projected AM0 efficiency of 20.1% is a combination of 13.8% for the top cell and 6.3% for the underlying CIGS cell. The top cell was altered by adding small amounts of zinc to the CdTe to produce a wider bandgap $Cd_{1-x}Zn_xTe$ with electronic properties approximately those of CdTe.

Results of the AMPS modelling were used to focus the research of USF on developing a high efficiency, high bandgap top cells of CdSe and CdZnTe.

Several key technologies are required to achieve high specific power thin-film solar arrays for space. To meet the target of a > 20% II-VI-based thin-film tandem structure on a flexible substrate, several processing steps must be mastered. These include the fabrication of top and bottom cells on thin flexible metal foils or polymers substrates. The top cell must be a high efficiency, wide bandgap cell, such as CuInGaS2, CdSe or CdZnTe. In order to produce a monolithic device, a junction diode will be required. We summarize the progress toward the development of the tandem thin-film solar cells in the next sections.

II-VI TOP CELL DEVICE FABRICATION

CdSe Devices With Transparent Conductors

CdSe material is potentially a wide bandgap component of high-efficiency, thin-film, tandem devices. In particular, we have initially targeted a 4-terminal structure that requires both front and rear transparent contacts. The first step is to demonstrate high-quality electronic absorbers. Once this is accomplished, the focus will shift to optimized transparent contacts. Thus the results reported below are for CdSe deposited on a transparent conductor; the other contact that is deposited on the CdSe is transparent as well.

Our primary means of evaluating electronic quality is to make devices and characterize their performance. In this case we are using a metal/window layer contact (WLC)/ CdSe/ transparent conductor (TC) structure. We are experimenting with several TCs such as ZnO, SnO, and Indium Tin Oxide (ITO), all degenerate n-type materials, with ZnSe and ZnTe as the potential p-type WLC. The metal is either Cu or Au with a thickness of 20 – 140 Å. Analysis of our devices indicates that they do not display MIS behavior; however, this does not detract from the utility of this structure for evaluating the CdSe absorber. What is unique about these structures is that they are deposited on transparent contacts. Results for such devices have not previously been reported in the literature to our knowledge.

Typical light and dark IV curves for these devices on transparent contacts are shown in Figure 3. What we focus on for evaluating the CdSe is the Jsc. Other aspects of these curves are discussed in previous publications.⁴ Proper determination of Jsc results from integrating QE spectra against reference cells calibrated by NREL.

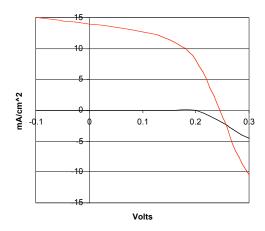


Figure 3. Dark and light IV curves for typical Cu/ZnSe/CdSe/TC devices

One example device (Cu thickness = 140 Å) had an integrated Jsc of 11.1 mA/cm². It is low because the Cu layer in this case is thick and absorbs a significant amount of light. Correcting for the transmission of the Cu/ZnSe layer results in increased generation efficiency for light that potentially would reach the CdSe layer. This is the internal QE and its integration results in the internal Jsc for the device. This is the appropriate term for evaluating the CdSe. In this case the internal Jsc is 18.3 mA/cm². Details of the optical considerations for these procedures were previously reported.⁴ The important point is that this current density is sufficient to achieve the project goals and demonstrates the high electronic quality of CdSe on a transparent substrate. AMPS simulations that project 25% efficiency for the tandem structure have Jsc's in the 18-19 mA/cm² for the CdSe device. The challenge at this point is to work with the contact layers to optimize transmission of as much light as possible to the CdSe layer.

A device with a 260 Å ZnSe layer and a 30 Å Cu layer allowed much more transmitted light; the resulting external Jsc is 14.7 mA/cm². This is noted to be considerably higher than the value of 12.8 mA/cm² for a 6.8% efficient device that was grown by MBE;⁵ this is the best device previously reported in the literature. We are thus convinced that CdSe grown on transparent contacts has the requisite properties to produce very high-efficiency tandem devices.

The next technical challenge is the development of transparent contacts. While the n-type contact should be straightforward, and may already be acceptable, the p-type contact is a formidable challenge. Fortunately, there is broad interest in developing such contacts for a variety of applications, thus there is significant worldwide effort. For example, development of p-type ZnSe was in large part responsible for the emergence of blue lasers. While ZnO, ZnSe, and ZnTe are all under consideration, ZnSe has been typically employed to evaluate CdSe (Cu/ZnSe/CdSe/TC).

Typical Voc's have been in the 250–300 mV range, but Voc generation has been determined by the Cu contact rather than the ZnSe. We are working to change this by developing doping procedures for the ZnSe. Recent devices with Cu/ZnTe are exhibiting Voc's approaching 500 mV. IV curves for Cu/ZnTe/CdSe/TC device structures are shown in Figure 4. As with the Cu/ZnSe devices light is incident from the TC side. As can be seen, Jsc is significantly lower than Cu/ZnSe devices.

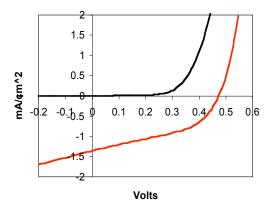


Figure 4. IV curves for Cu/ZnTe/CdSe/TC structures

The ZnTe thickness in this case is 0.4 $\square m$, considerably thicker than needed. By comparison the ZnSe thickness is typically about 200 Å. Thus far we have found it necessary to make the ZnTe this thick to get working devices. There seems to be some difficulty in attaining complete absorber coverage and avoiding pinholes if we reduce the thickness. The thickness of the ZnTe layer is likely causing a significant downshift in QE. This is in addition to the loss in blue QE relative to ZnSe because of the narrower bandgap (2.39 eV) relative to that of ZnSe (2.83 eV). We are working to lower the thickness to recover these losses. AMPS simulations also suggest that unfavorable band offsets can lead to lowering of QE. We are following up on these insights as well

What is most encouraging is the significant increase in Voc. As seen in Figure 4, Voc's are up to 475 mV, about a 175 mV increase over typical Cu/ZnSe window layer devices. This increase is due to a larger effective contact energy for Cu/ZnTe. This is not surprising in that ZnTe is known to be more ptype prone than ZnSe. However, it does demonstrate that if we can move the contact energy down in ZnSe, concomitant increases in Voc should ensue. ZnTe is more readily p-type than ZnSe, and preliminary analysis of these devices suggests that Voc is starting to be controlled by the ZnTe layer itself rather than the Cu – a desired result. We are thus encouraged that further development of these contacts will lead to achievement of our goals.

CZT Junctions and Solar Cells

Cadmium zinc telluride films (CZT) afford the opportunity to tune the bandgap of this material from 1.45 to 2.26 eV making it an excellent candidate for tandem solar cell applications. In order to investigate the potential of this material, two deposition technologies are being employed: (a) co-sputtering

from CdTe and ZnTe targets, and (b) co-close-spaced sublimation (CCSS) from CdTe and ZnTe powders. These two technologies provide a wide range of deposition conditions to evaluate these films and their junctions. Typically the deposition temperatures for sputtering processes are lower than those used for sublimation, and also the grain size of sputtered films is smaller.

One of the most challenging aspects of these efforts was associated with the CCSS method. Reproducibility and compositional uniformity were initially a challenge. However, after partially optimizing the process (source and substrate temperatures, source material, spacing, and pressure) the variations associated with films produced with this method were well within acceptable limits. The targeted Zn composition for this film was 30%. The increase of Zn at the edges is expected because of the particular source design currently utilized. Films deposited by co-sputtering have been found to be very uniform and reproducible. Figure 5 shows the composition of CZT films deposited by CCSS as a function of the bandgap determined from optical transmission measurements. The solid lines represent data obtained from the literature. 6.7 The Zn content of the CCSS films shown in Figure 5 was obtained from measurements (squares) and measurements (diamonds). As the data indicates there exists a small uncertainty in our composition measurements, but in general our results are in good agreement with the literature.

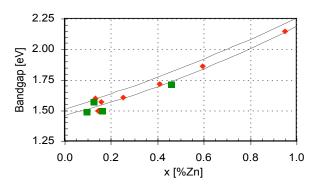


Figure 5. E_G vs. Zn content of CZT film

XRD measurements also indicated that the films did not contain any secondary phases of CdTe or ZnTe as shown in Figure 6. Although the CZT film with 41% Zn in the figure exhibits preferential orientation, in many other instances studied to-date, CZT films have exhibited nearly random orientation. The CZT films consist of rather large grains, typically larger than 1 □m, however, they also contain a significant fraction of smaller grains (less

than 1 \square m) resulting in non-uniform grain size distribution, as indicated in Figure 7; it is not clear if this is detrimental to device performance.

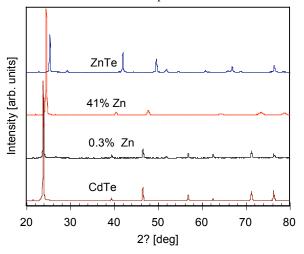


Figure 6. XRD spectra of CdTe (bottom), ZnTe (top) and CZT films.

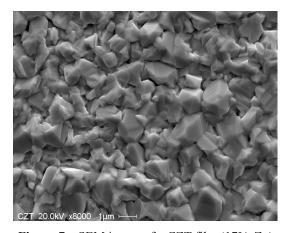


Figure 7. SEM image of a CZT film (17% Zn).

A structure similar to the CdTe superstrate configuration was initially used for cell fabrication: glass/SnO₂/CdS/CZT/graphite. Variations to this have included the use of alternative window materials such as ZnSe, and back contacts such as ZnTe/Cu, as well as substrate structures on metal foil substrates. The targeted bandgap for CZT is 1.7 eV, although, due to process control issues this has varied from 1.6 to 1.95 eV. To-date results point to a significant limitation in CZT-based solar cells: low $J_{\rm SC}$'s. At this time it appears that this is most likely related to the absorber (CZT) being highly defective leading to poor collection. In many cases $J_{\rm SC}$ is limited to about 20% of the expected $J_{\rm SC}$ value based on the bandgap of the material. The efforts to improve $J_{\rm SC}$ and in

general the overall performance of these devices have focused on utilizing post-deposition heat treatments, similar to the approach used with CdTe solar cells. Another unknown factor at this time is the role of the CZT/CdS interface. In CdTe/CdS junctions, it is well known that the formation of CdS_{1-x}Te_x at the interface results in improved performance. Typical solar cell parameters for CZT/CdS solar cells are listed in table 1, where V_{OC} 's in excess of 700 mV have been obtained, with J_{SC} 's limited to values below 2 mA/cm². In order for CZT to reach the performance required of a top cell in a tandem structure, these poor collection characteristics must be overcome.

Table 1. V_{OC} & FF for SnO₂/CdS/CZT/ZnTe devices.

Sample#	E _G		V _{oc}	J_{SC}
	[eV]		[mV]	[mA/cm ²]
		High	780	1.40
7-26-5-2	1.72	Low	720	0.80
		Average	743	1.11
		High	720	2.00
7-26-5-1	1.72	Low	690	1.56
		Average	700	1.78

Efforts to improve collection have focused on post-deposition heat treatments of CZT. Figure 8 shows the effect of H_2 annealing on spectral response of a CZT device. This demonstrates that the properties of CZT can be improved through post-processing treatments while maintaining the asdeposited bandgap of films. The highest J_{SC} measured to-date is $\sim 10~\text{mA/cm}^2$, for E_G =1.65 eV, approximately 50% of expected value for this bandgap. Our focus is improving the electronic properties of CZT itself. Various window materials are routinely incorporated into solar cell structures in order to identify the most effective window partner. Work continues on transparent p-type contacts.

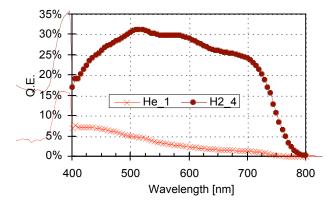


Figure 8. Spectral response of CZT solar cells heat treated in inert and H₂ ambient.

THIN-FILM CELLS ON METAL FOILS

CuIn_{1-x}Ga_xS₂ Thin Film Solar Cells

An alternative to the II-VI-based top cell materials described above is CuInS₂ (CIS2). The bandgap can be increased to 1.75 eV with gallium substitutioned for In of 0.3 (CuIn_{0.7}Ga_{0.3}S₂, generically referred to as CIGS2). Processing consists of sulfurization of stacked Cu-In-Ga metallic precursor layers by conventional annealing in H₂S. The specific objective of this approach is to develop wide bandgap CIGS2 solar cells for use as top cell, narrow bandgap CIGS as bottom cell, and p-type transparent conducting layers for fabrication of high performance, two-terminal, two-junction, tandem thin film solar cells on ultra-lightweight metallic foils.

In earlier work, deposition parameters were optimized for achieving high-efficiency solar cells on 1.25" x 1" glass and flexible foil substrates.8 Substrates included 127 \(\square\) and 20 \(\square\) thick brightannealed stainless steel (SS) foils and 25 [m thick titanium foils. Results reported were for cells deposited on 127 [m thick SS foils. CuGa and In precursor layers were DC magnetron-sputter deposited on Mo-coated SS foils with elemental ratio Cu/(In+Ga) of ~1.4. The best conversion efficiency measured at NREL (AM1.5) of solar cells completed using Cu-poor CIGS2 layers on stainless steel foils had PV parameters: $V_{oc} = 763 \text{ mV}$, $J_{sc} = 20.26$ mA/cm^2 , FF = 67.04%, $\Pi = 10.4\%$ (Figure 9). PV parameters of the best CIGS2 solar cell measured at NASA GRC (AM0) were $V_{oc} = 802.9 \text{ mV}$, $J_{sc} = 25.07$ mA/cm^2 , FF = 60.06%, and $\square = 8.84\%$.

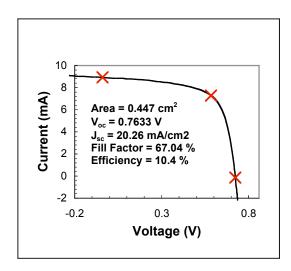


Figure 9. AM1.5 I-V characteristics of a CIGS2 cell on SS foil.

Scale-up of this process is required in order to produce cells of sufficient area to provide power for space missions. Therefore, two large vacuum systems were designed and constructed (Figure 10). The larger vacuum system has a 40"x18"x8" chamber fitted with three 4"x12" DC magnetron sputtering sources for deposition of Mo, In, and Cu_{0.78}Ga_{0.22} thin films; the smaller system has a 29"x18"x8" chamber fitted with two 4"x12" RF magnetron sputtering sources for deposition of transparent, conducting ZnO and ZnO:Al.



Figure 10. Large area sputtering vacuum systems

Stainless steel mechanisms were installed for linear substrate movement in both the chambers. Substrates can be moved in small steps parallel to the 4" width of the target at a fixed interval to achieve integral and uniform film thickness in the direction of movement. A modified magnetic array in which the magnetic field at the extremities was boosted by introducing strong magnets at and near the periphery resulted in thickness uniformity for Mo (DC) and ZnO (RF) as shown in Figure 11. This will facilitate deposition of large area (6"x4") thin film solar cells.

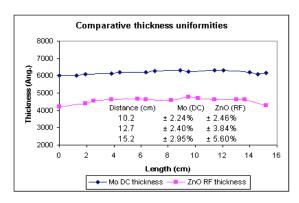


Figure 11. Thickness variation plot for DC and RF magnetron sputtering sources.

Large-Area CIGS Thin Film Solar Cells

CIGS solar cells will be competitive with existing cell technologies if they demonstrate the following: (i) 1000 W/kg at the component level (vs. 250-350 W/kg for III-V& Si, respectively); (ii) moderate power densities of >170 W/m² (vs. 170-300 W/m² for Si & III-V B.O.L, respectively); (iii) superior radiation tolerance (EOL/BOL = 0.85-0.90 vs. 0.70-0.80 for III-V & Si, respectively); (iv) equivalent connectivity for producing "supercell" or sub-array assemblies; (v) \$20-30/W projected production costs (vs. \$130-270/W for Si and III-V cells, respectively); and (vi) provide equivalent or superior reliability for various orbital configurations.

Furthermore, in order to demonstrate manufacturing scale, or "large-area" CIGS absorber deposition capability, the following must be achieved: (i) deposition uniformity (quantified by cell performance) for areas ranging from 1000-3000 cm²; (ii) run-run reproducibility and yield; and (iii) system throughput and cost considerations.

DayStar is proposing an alternative approach that could provide for a substantially higher probability of success. These include the use of durable metal substrates (in contrast to *plastic*), dedicated batch processing for space products (in contrast to *roll-to-roll*), simple and previously qualified interconnect schemes (in contrast to monolithic integration), and proven deposition processes.

Cu(In,Ga)Se₂ thin-films were deposited by thermal co-evaporation of the elements under high vacuum (substrate temperatures can reach 600°C). The work involved in establishing uniform, reproducible delivery of each constituent metal was substantial. It first involved achieving compatibility between furnace material and source material type and temperature requirements. Subsequent to source temperature – rate calibrations, the uniformity of the film deposition had to be established for each source.

Upon realization of individual film uniformity and reproducibility (which often required revisiting), the development effort turned to making CIGS films of useful quality for photovoltaic devices. In order to characterize uniformity across the substrate or deposition area, either a single layer film was made, or the standard 2-stage process for making device quality absorbers was employed. A critical issue that is considered in this process is the retention of a virgin surface on which to evaporate the initial layers of the CIGS absorber. It is believed that Na on the Mo surface prior to the CIGS layer deposition compromises adhesion of the film. Further details of the processing of other layers such as heterojunction. TCO, and contacts can be found in previous publications.9

Film characterization is accomplished by several analysis methodologies. Film morphology is examined by scanning electron microscopy (SEM, see Figure 12). SEM depicts the desired grain and film morphology for high efficiency devices. Film stoichiometry, as a function of depth, is obtained by Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS). In Figure 13, a typical SIMS depth profile is shown for a CIGS sample.

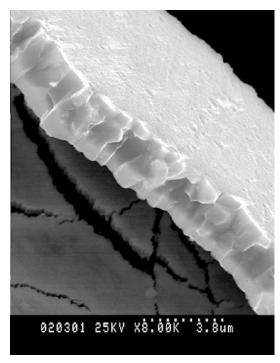


Figure 12. SEM of CIGS thin-film sample fabricated on metal substrate.

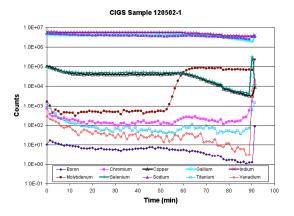
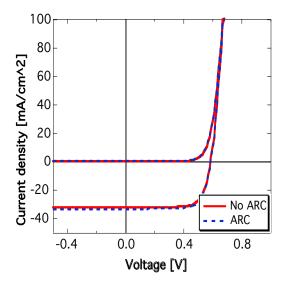


Figure 13. SIMS depth profile for CIGS sample.

Completed devices were characterized by current-voltage (I-V) under simulated AM1.5 illumination, internal and external quantum efficiency (QE) across the spectral region of interest, and by laser-beam induced current (LBIC) measurements. Figure 14 presents I-V measurements of 4-cm² (top) and 32-cm² (bottom) CIGS devices both with and without anti-reflective coatings (ARC). Data for these samples are presented in Table 2.



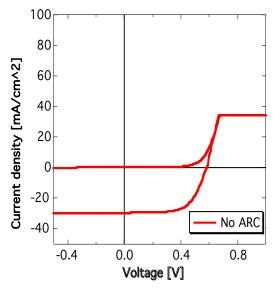


Figure 14. I-V measurements of 4-cm² (top) and 32-cm² (bottom) CIGS devices.

Table 2. Performance Data for CIGS Devices.

Area	ARC	V _{oc} (mV)	J _{sc} (mA/cm ²	FF	η
4-cm ²	No	587	32.4	74.6	14.2
	Yes	588	33.5	74.4	14.7
32-cm ²	No	583	29.8	63.9	11.1

LOW-TEMPERATURE SPRAY CVD PROCESS

A key step for device fabrication for thin film solar cells is the deposition onto flexible, lightweight substrates such as polyimides. As discussed above, current methods for depositing ternary crystallite compounds include co-evaporation of elements or alloys, reactive sputtering or flash evaporation, which are often followed by toxic sulphurization/ selenization steps, at elevated temperatures. Furthermore, under these conditions loss of volatile In/Ga chalcogenides is common. The high temperature requirements make this protocol incompatible with all presently known flexible polyimides, or other polymer substrates. In addition, the use of toxic reagents is a limiting factor. The use of multi-source inorganic/organometallic precursors in a chemical vapor deposition (CVD)-type process is appealing due to milder process parameters. However, stoichiometric control of deposited films can be difficult to achieve; and film contamination has been reported. A novel alternative approach is use of ternary single source precursors (SSP's) which have the I-III-VI2 stoichiometry "built in" and are suitable for low temperature deposition (Figure 15).¹⁰

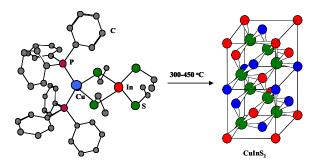


Figure 15. Pyrolysis of SSP [{PPh₃}₂Cu(SEt)₂-In(SEt)₂], to produce CuInS₂.

In the course of our investigations for improved single source precursors for the spray CVD of chalcopyrite thin-films of one of the Cu(Ga:In)(Se:S)₂ (CIGSS) semiconductors, we have continued to expand the molecular design of SSP

based on the $[\{LR_3\}_2Cu(ER')_2M(ER')_2]$ architecture [where L = P, As, Sb; E = S or Se; M = In or Ga]. This is primarily due to the limited studies on preparation and investigation for their use in a spray CVD process. Furthermore, the number of "tunable" sites within the complex allows for their use in preparing a number of chalcopyrites of varying composition (derived from the CIGSS structure) in addition to engineer the SSP to match a given spray CVD process (see example in Figure 15).

Spray CVD is a useful technique where a room-temperature precursor solution is ultrasonically nebulized, and is swept into a two-zone, hot-wall reactor (Figure 16). The carrier-solvent is evaporated in the warm zone, and the gaseous precursors are decomposed in the hot zone, where film growth occurs as in conventional CVD. Spray CVD maintains the most desirable features of metal organic (MO)CVD and spray pyrolysis, such as film growth in inert atmospheres, large area deposition, laminar flow over the substrate, and low temperature solution reservoir, while avoiding the major difficulties of each. It minimizes the high volatility and temperature requirements for the precursor, which are essential in MOCVD, by delivering the precursor to the furnace as an aerosol propelled by a fast-flowing carrier gas from a low-temperature precursor reservoir analogous to that employed in spray pyrolysis. The latter feature is an important benefit that can prevent premature precursor decomposition when using thermally labile precursors. An example of the use of a compound from this family of precursors is included.

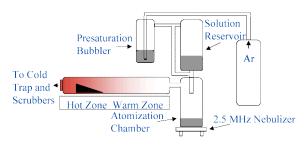


FIGURE 16. Schematic for spray CVD apparatus.

The ability of the new precursors to thermally decompose to yield single-phase CIS was investigated by powder X-ray diffraction (XRD) analysis and energy dispersive spectroscopy, (EDS) on the non-volatile solids from the thermal experiments of selective compounds. The onset for decomposition of [{P(n-Bu)₃}₂Cu(SEt)₂In(SEt)₂] (1), a liquid at room temperature, was 264°C, and reduced by 80°C under vacuum. XRD spectra for the non-volatile material produced from the pyrolysis of

1 with the JCPDS reference patterns for CuInS₂ (27-0159), confirmed it to be single-phase CuInS₂ (Figure 17). Examination of the EDS spectra for the same samples shows predominant emissions due to Cu, In, and S edges, with the approximate percentage atomic composition of 27, 23 and 50 for 1. Well adhering films of CuInS₂ were deposited on a Mo foil substrate by spray CVD at 390°C using 1 were dark blue/black, due to variation in film thickness. As deposited, the CuInS₂ film is highly (112) oriented (Figure 18).

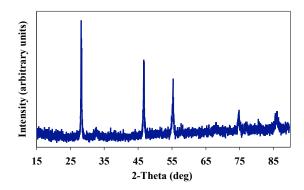


FIGURE 17. XRD for non-volatile residue from pyrolysis of **1**. Peaks from left are: 112, 204/220, 312, 332, 424.

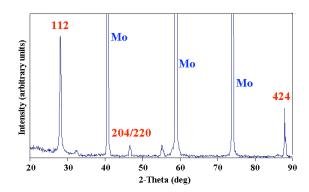


FIGURE 18. X-ray powder diffraction spectra of a CuInS₂ thin film on Mo using 1.

Spray CVD using SSP's is a mild, simple, clean, and scalable technique for depositing CIGSS thinfilms on flexible polymer substrates at reduced temperatures. Spray CVD has a number of tunable variables, such as flow-rate, concentration, solvent polarity, which is advantageous to achieve the desired film characteristics. An in-dept study is underway to address the correlation of these parameters to film composition and to exploit these insights to produce optimized thin film cells.¹¹

THIN FILM SYSTEMS ANALYSIS

Thin film solar arrays built on ultra-lightweight substrates hold considerable promise as an enabling technology for future space missions requiring very large specific power and small launch stowed volume. As thin film solar cell technologies near reality, a number of system studies have been undertaken in recent years. 12,13 System studies of emerging technologies are often used to make the crucial selection decisions between competing technologies. In order to fully understand the conclusions of each study, it is necessary to examine the underlying constraints inherent in each study and to determine the impact of each constraint on the study's conclusions. Understanding the underlying constraints of a study is even more important for studies comparing emerging technologies to wellestablished technologies such as comparing thin film solar cell technologies to crystalline solar cell technologies.

A recent study compared existing and near-term array structures populated with crystalline multijunction solar cells to the same array structures populated with thin film solar cells.¹³ This study was an excellent effort; however, the constraints inherent in the study need to be factored into the interpretation of the study's conclusions. For example, since the study focused on existing or near-term array structures originally designed for crystalline solar cells that are significantly denser and more rigid than thin film solar cells on lightweight flexible substrates, array design constraints such as stiffness were carried over to the thin film configurations. While this constraint would be appropriate for rigid crystalline solar arrays, it limits the applicability of the study results for lightweight, flexible thin film solar arrays. This also demonstrates the need to revisit the spacecraft requirements when setting constraints for advanced system studies. Where stiffness was a logical constraint for rigid, crystalline solar arrays, would momentum transfer to the spacecraft be a better metric for very lightweight, flexible thin film array structures?

CONCLUSIONS

Significant progress has been made in the development of thin film solar cells on very lightweight, flexible substrates. A single-source precursor deposition process that will enable the deposition of CIS on a variety of polymers has been demonstrated with controlled grain size and improved quality. Progress has been made in the development of a compatible top cell.

The evaluations of thin film array studies have provided opportunities for the creation of a thin-film, device technologies that will be of interest to satellite manufacturers and enable future space missions.

REFERENCES

- 1. S.G. Bailey and D.J. Flood, *Progress in Photovoltaics* **6**, 1 (1998).
- 2. P.A. Iles, Solar Energy Materials and Solar Cells 68, 1 (2001).
- 3. A.F. Hepp, et al., "Multi-Junction Thin-Film Solar Cells on Flexible Substrates for Space Power," *Proceedings of the 37th Intersociety Energy Conversion Engineering Conference*, IECEC, New York, NY (2002).
- 4. P. Mahawela, S. Jeedigunta, C. S. Ferekides, and D. L. Morel, *Thin Solid Films*, in press.
- 5. P. Gashin, A. Focsha, T. Potlog, A. Simashkevich, and V. Leondar, *Solar Energy Materials and Solar Cells* **46**, 323 (1997).
- 6. D. J. Olego, J. P. Faurie, S. Sivananthan, and P. M. Raccah, *Appl. Phys. Lett.* **47**, 1172 (1985).
- 7. S. M. Johnson, S. Sen, W. H. Konkel, M. H. Kalisher, *J. Vac. Sci. Technol.* **B9**, 1897 (1991).
- 8. N.G. Dhere, S.R. Ghongadi, M.B. Pandit, A.A. Kadam, A.H. Jahagirdar, and V.S. Gade, "AFM, Micro-PL, and PV Analyses OF CuIn_{1-x}Ga_xS₂ Thin Film Solar Cells on Stainless Steel Foil," *Proceedings of the 29th IEEE PV Specialist Conference*, IEEE, New York, NY (2002).
- 9. J.R. Tuttle, A. Szalaj, and J. Keane, "A 15.2% AM0/1433 W/Kg Thin-Film Cu(In,Ga)Se₂ Solar Cell for Space Applications," *Proceedings of the 28th IEEE PV Specialist Conference*, IEEE, New York, NY (2000).
- 10. K.K. Banger, J.A. Hollingsworth, J.D. Harris, J. Cowen, W.E. Buhro, and A.F. Hepp, *Appl. Organometal. Chem.* **16**, 617 (2002).
- M.H.-C. Jin, K.K. Banger, J.D. Harris, and A.F. Hepp, "The Effect of Film Composition on the Texture and Grain Size of CuInS₂ Prepared by Chemical Spray Pyrolysis," *Mater. Res. Soc. Proc.* 763, MRS, Pittsburgh, PA (2003).
- 12. D.J. Hoffman, et al., "Thin-Film Photovoltaic Solar Array Parametric Assessment," *Proceedings of the 35th Intersociety Energy Conversion Engineering Conference*, IECEC, New York, NY (2000).
- 13. D. M. Murphy, et al., "Thin-Film and Crystalline Solar Cell Array System Performance Comparisons," *Proceedings of the 29th IEEE PV Specialist Conference*, IEEE, New York, NY (2002).

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13. ABSTRACT (Maximum 200 words)

The thin-film solar cell program at NASA GRC is developing solar cell technologies for space applications which address two critical metrics: specific power (power per unit mass) and launch stowed volume. To be competitive for many space applications, an array using thin film solar cells must significantly increase specific power while reducing stowed volume when compared to the present baseline technology utilizing crystalline solar cells. The NASA GRC program is developing two approaches. Since the vast majority of the mass of a thin film solar cell is in the substrate, a thin film solar cell on a very lightweight flexible substrate (polymer or metal films) is being developed as the first approach. The second approach is the development of multijunction thin film solar cells. Total cell efficiency can be increased by stacking multiple cells having bandgaps tuned to convert the spectrum passing through the upper cells to the lower cells. Once developed, the two approaches will be merged to yield a multijunction, thin film solar cell on a very lightweight, flexible substrate. The ultimate utility of such solar cells in space require the development of monolithic interconnections, lightweight array structures, and ultra-lightweight support and deployment techniques.

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